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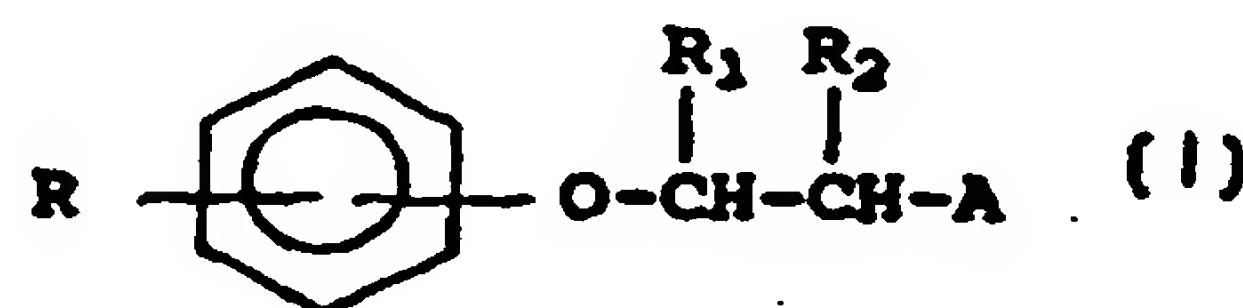
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<p>(21) International Application Number: PCT/US97/07991 (22) International Filing Date: 12 May 1997 (12.05.97) (30) Priority Data: 08/645,992 14 May 1996 (14.05.96) US (71) Applicant: CHEVRON CHEMICAL COMPANY (US/US); P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventor: CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US). (74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p>		<p>(81) Designated States: AU, BR, CA, CN, JP, KR, MX, NZ, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: POLYALKYLPHENOXYAMINOALKANES AND FUEL COMPOSITIONS CONTAINING THE SAME

(57) Abstract

Polyalkylphenoxyaminoalkanes having formula (I), wherein R is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000; R₁ and R₂ are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and A is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms. The compounds of formula (I) are useful as fuel additives for the prevention and control of engine deposits.



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01 POLYALKYLPHENOXYAMINOALKANES
02 AND FUEL COMPOSITIONS CONTAINING THE SAME

03
04 BACKGROUND OF THE INVENTION

05
06 Field of the Invention

07
08 This invention relates to novel
09 polyalkylphenoxyaminoalkanes. In a further aspect,
10 this invention relates to the use of these compounds
11 in fuel compositions to prevent and control engine deposits.

12
13 Description of the Related Art

14
15 It is well known that automobile engines tend to form
16 deposits on the surface of engine components, such as
17 carburetor ports, throttle bodies, fuel injectors, intake
18 ports and intake valves, due to the oxidation and
19 polymerization of hydrocarbon fuel. These deposits, even
20 when present in relatively minor amounts, often cause
21 noticeable driveability problems, such as stalling and poor
22 acceleration. Moreover, engine deposits can significantly
23 increase an automobile's fuel consumption and production of
24 exhaust pollutants. Therefore, the development of effective
25 fuel detergents or "deposit control" additives to prevent or
26 control such deposits is of considerable importance and
27 numerous such materials are known in the art.

28
29 For example, aliphatic hydrocarbon-substituted phenols are
30 known to reduce engine deposits when used in fuel
31 compositions. U.S. Patent No. 3,849,085, issued
32 November 19, 1974 to Kreuz et al., discloses a motor fuel
33 composition comprising a mixture of hydrocarbons in the
34 gasoline boiling range containing about 0.01 to 0.25 volume

01 percent of a high molecular weight aliphatic
02 hydrocarbon-substituted phenol in which the aliphatic
03 hydrocarbon radical has an average molecular weight in the
04 range of about 500 to 3,500. This patent teaches that
05 gasoline compositions containing minor amounts of an
06 aliphatic hydrocarbon-substituted phenol not only prevent or
07 inhibit the formation of intake valve and port deposits in a
08 gasoline engine, but also enhance the performance of the
09 fuel composition in engines designed to operate at higher
10 operating temperatures with a minimum of decomposition and
11 deposit formation in the manifold of the engine.

12

13 U.S. Patent No. 4,259,086, issued March 31, 1981 to
14 Machleder et al., discloses a detergent additive for fuels
15 and lubricating oils which comprises the reaction product of
16 an aliphatic hydrocarbon-substituted phenol, epichlorohydrin
17 and a primary or secondary monoamine or polyamine. In
18 addition, U.S. Patent No. 4,048,081, issued September 13,
19 1977 to Machleder et al., discloses a detergent additive for
20 gasoline which is the reaction product of a polyisobutene
21 phenol with epichlorohydrin, followed by amination with
22 ethylene diamine or other polyamine.

23

24 Similarly, U.S. Patent No. 4,134,846, issued January 16,
25 1979 to Machleder et al., discloses a fuel additive
26 composition comprising a mixture of (1) the reaction product
27 of an aliphatic hydrocarbon-substituted phenol,
28 epichlorohydrin and a primary or secondary mono- or
29 polyamine, and (2) a polyalkylene phenol. This patent
30 teaches that such compositions show excellent carburetor,
31 induction system and combustion chamber detergency and, in
32 addition, provide effective rust inhibition when used in
33 hydrocarbon fuels at low concentrations.

34

01 Amino phenols are also known to function as
02 detergents/dispersants, antioxidants and anti-corrosion
03 agents when used in fuel compositions. U.S. Patent
04 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for
05 example, discloses amino phenols having at least one
06 substantially saturated hydrocarbon-based substituent of at
07 least 30 carbon atoms. The amino phenols of this patent are
08 taught to impart useful and desirable properties to
09 oil-based lubricants and normally liquid fuels.

10
11 In addition, polybutylamines have been taught to be useful
12 for preventing deposits in the intake system of internal
13 combustion engines. For example, U.S. Patent No. 4,832,702,
14 issued May 23, 1989 to Kummer et al., discloses fuel and
15 lubricant compositions containing polybutyl or
16 polyisobutylamine additives prepared by hydroformulating a
17 polybutene or polyisobutene and then subjecting the
18 resulting oxo product to a Mannich reaction or amination
19 under hydrogenating conditions.

20
21 Polyether amine fuel additives are also well known in the
22 art for the prevention and control of engine deposits.
23 These polyether additives have a polyoxyalkylene "backbone",
24 i.e., the polyether portion of the molecule consists of
25 repeating oxyalkylene units. U.S. Patent No. 4,191,537,
26 issued March 4, 1980 to Lewis et al., for example, discloses
27 a fuel composition comprising a major portion of
28 hydrocarbons boiling in the gasoline range and from 30 to
29 2,000 ppm of a hydrocarbyl polyoxyalkylene aminocarbamate
30 having a molecular weight from about 600 to 10,000, and at
31 least one basic nitrogen atom. The hydrocarbyl
32 polyoxyalkylene moiety is composed of oxyalkylene units
33 having from 2 to 5 carbon atoms in each oxyalkylene unit.
34 These fuel compositions are taught to maintain the

01 cleanliness of intake systems without contributing to
02 combustion chamber deposits.
03
04 Aromatic compounds containing a poly(oxyalkylene) moiety are
05 also known in the art. For example, the above-mentioned U.S.
06 Patent No. 4,191,537, discloses alkylphenyl
07 poly(oxyalkylene) polymers which are useful as intermediates
08 in the preparation of alkylphenyl poly(oxyalkylene)
09 aminocarbamates.
10
11 Similarly, U.S. Patent No. 4,881,945, issued November 21,
12 1989 to Buckley, discloses a fuel composition comprising a
13 hydrocarbon boiling in the gasoline or diesel range and from
14 about 30 to about 5,000 parts per million of a fuel soluble
15 alkylphenyl polyoxyalkylene aminocarbamate having at least
16 one basic nitrogen and an average molecular weight of about
17 800 to 6,000 and wherein the alkyl group contains at least
18 40 carbon atoms.
19
20 U.S. Patent No. 5,112,364, issued May 12, 1992 to Rath et
21 al., discloses gasoline-engine fuels which contain small
22 amounts of a polyetheramine and/or a polyetheramine
23 derivative, wherein the polyetheramine is prepared by
24 reductive amination of a phenol-initiated or alkylphenol-
25 initiated polyether alcohol with ammonia or a primary amine.
26
27 European Patent Application Publication No. 310,875,
28 published April 12, 1989 discloses fuels for spark ignition
29 engines containing a polyetheramine additive prepared by
30 first propoxylating and/or butoxylating an alkanol or
31 primary or secondary alkylmonoamine and then aminating the
32 resulting polyether with ammonia or a primary aliphatic
33 amine.
34

01 French Patent No. 2,105,539, published April 28, 1972,
02 discloses carburetor detergent additives which are
03 phenoxypropylamines which may be substituted with up to five
04 hydrocarbon radicals of 1 to 30 carbon atoms on the aromatic
05 ring. This patent also discloses additives obtained by
06 reacting such phenoxypropylamines with alkylphosphoric
07 acids.

08

09

SUMMARY OF THE INVENTION

10

11 I have now discovered certain polyalkylphenoxyaminoalkanes
12 which provide excellent control of engine deposits,
13 especially intake valve deposits, when employed as fuel
14 additives in fuel compositions.

15

16 The compounds of the present invention include those having
17 the following formula and fuel soluble salts thereof:

18

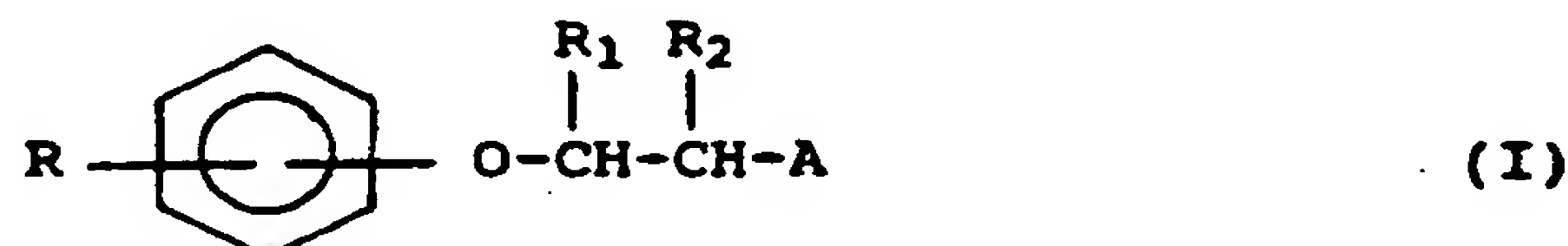
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23



24 wherein R is a polyalkyl group having an average molecular
25 weight in the range of about 600 to 5,000;

26

27 R₁ and R₂ are independently hydrogen or lower alkyl having 1
28 to 6 carbon atoms; and

29

30 A is amino, N-alkyl amino having about 1 to about 20 carbon
31 atoms in the alkyl group, N,N-dialkyl amino having about 1
32 to about 20 carbon atoms in each alkyl group, or a polyamine
33 moiety having about 2 to about 12 amine nitrogen atoms and
34 about 2 to about 40 carbon atoms.

01 The present invention further provides a fuel composition
02 comprising a major amount of hydrocarbons boiling in the
03 gasoline or diesel range and a deposit-controlling effective
04 amount of a compound of the present invention.

05

06 The present invention additionally provides a fuel
07 concentrate comprising an inert stable oleophilic organic
08 solvent boiling in the range of from about 150°F. to 400°F.
09 and from about 10 to 70 weight percent of a compound of the
10 present invention.

11

12 Among other factors, the present invention is
13 based on the surprising discovery that certain
14 polyalkylphenoxyaminoalkanes provide excellent
15 control of engine deposits, especially on intake valves,
16 when employed as additives in fuel compositions.

17

18 DETAILED DESCRIPTION OF THE INVENTION

19

20 The polyalkylphenoxyaminoalkanes of the present invention
21 have the general formula:

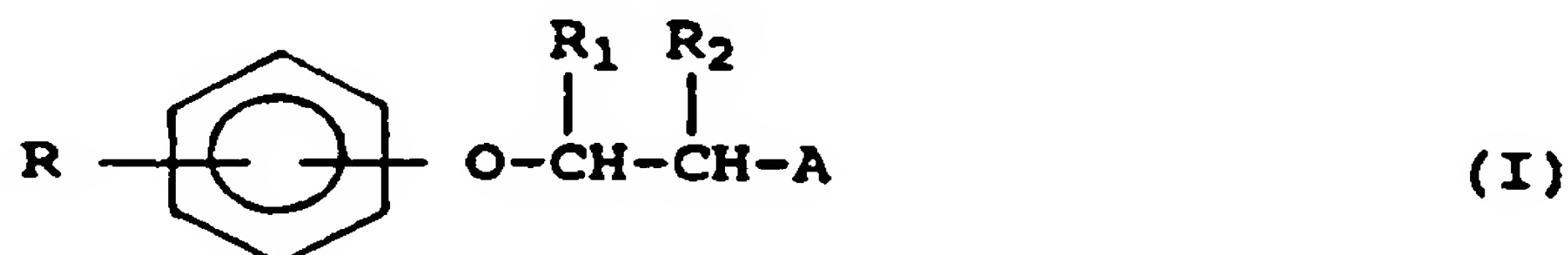
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27

28

wherein R, R₁, R₂ and A are as defined above.

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Preferably, R is a polyalkyl group having an average
molecular weight in the range of about 600 to 3,000, more
preferably about 700 to 3,000, and most preferably about 900
to 2,500.

01 Preferably, one of R₁ and R₂ is hydrogen or lower alkyl of 1
02 to 4 carbon atoms, and the other is hydrogen. More
03 preferably, one of R₁ and R₂ is hydrogen, methyl or ethyl,
04 and the other is hydrogen. Most preferably, R₂ is hydrogen,
05 methyl or ethyl, and R₁ is hydrogen.

06

07 In general, A is amino, N-alkyl amino having from about 1 to
08 about 20 carbon atoms in the alkyl group, preferably about 1
09 to about 6 carbon atoms, more preferably about 1 to about 4
10 carbon atoms; N,N-dialkyl amino having from about 1 to about
11 20 carbon atoms in each alkyl group, preferably about 1 to
12 about 6 carbon atoms, more preferably about 1 to about 4
13 carbon atoms; or a polyamine moiety having from about 2 to
14 about 12 amine nitrogen atoms and from about 2 to about 40
15 carbon atoms, preferably about 2 to 12 amine nitrogen atoms
16 and about 2 to 24 carbon atoms. More preferably, A is amino
17 or a polyamine moiety derived from a polyalkylene polyamine,
18 including alkylene diamine. Most preferably, A is amino or
19 a polyamine moiety derived from ethylene diamine or
20 diethylene triamine.

21

22 It is preferred that the R substituent is located at the
23 meta or, more preferably, the para position on the aromatic
24 ring, i.e., para or meta relative to the ether group.

25

26 The compounds of the present invention will generally have a
27 sufficient molecular weight so as to be non-volatile at
28 normal engine intake valve operating temperatures (about
29 200°-250°C.). Typically, the molecular weight of the
30 compounds of this invention will range from about 700 to
31 about 3,500, preferably from about 700 to about 2,500.

32

33

34

01 Fuel-soluble salts of the compounds of formula I can be
02 readily prepared for those compounds containing an amino or
03 substituted amino group and such salts are contemplated to
04 be useful for preventing or controlling engine deposits.
05 Suitable salts include, for example, those obtained by
06 protonating the amino moiety with a strong organic acid,
07 such as an alkyl- or arylsulfonic acid. Preferred salts are
08 derived from toluenesulfonic acid and methanesulfonic acid.

09

10 Definitions

11

12 As used herein, the following terms have the following
13 meanings unless expressly stated to the contrary.

14

15 The term "amino" refers to the group: $-NH_2$.

16

17 The term "N-alkylamino" refers to the group: $-NHR_a$ wherein
18 R_a is an alkyl group. The term "N,N-dialkylamino" refers to
19 the group: $-NR_bR_c$, wherein R_b and R_c are alkyl groups.

20

21 The term "hydrocarbyl" refers to an organic radical
22 primarily composed of carbon and hydrogen which may be
23 aliphatic, alicyclic, aromatic or combinations thereof,
24 e.g., aralkyl or alkaryl. Such hydrocarbyl groups are
25 generally free of aliphatic unsaturation, i.e., olefinic or
26 acetylenic unsaturation, but may contain minor amounts of
27 heteroatoms, such as oxygen or nitrogen, or halogens, such
28 as chlorine.

29

30 The term "alkyl" refers to both straight- and branched-chain
31 alkyl groups.

32

33

34

01 The term "lower alkyl" refers to alkyl groups having 1 to
02 about 6 carbon atoms and includes primary, secondary and
03 tertiary alkyl groups. Typical lower alkyl groups include,
04 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
05 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

06
07 The term "polyalkyl" refers to an alkyl group which is
08 generally derived from polyolefins which are polymers or
09 copolymers of mono-olefins, particularly 1-mono-olefins,
10 such as ethylene, propylene, butylene, and the like.
11 Preferably, the mono-olefin employed will have 2 to about
12 24 carbon atoms, and more preferably, about 3 to 12 carbon
13 atoms. More preferred mono-olefins include propylene,
14 butylene, particularly isobutylene, 1-octene and 1-decene.
15 Polyolefins prepared from such mono-olefins include
16 polypropylene, polybutene, especially polyisobutene, and the
17 polyalphaolefins produced from 1-octene and 1-decene.

18
19 The term "fuel" or "hydrocarbon fuel" refers to normally
20 liquid hydrocarbons having boiling points in the range of
21 gasoline and diesel fuels.

22
23 General Synthetic Procedures

24
25 The polyalkylphenoxyaminoalkanes of this invention may be
26 prepared by the following general methods and procedures.
27 It should be appreciated that where typical or preferred
28 process conditions (e.g., reaction temperatures, times, mole
29 ratios of reactants, solvents, pressures, etc.) are given,
30 other process conditions may also be used unless otherwise
31 stated. Optimum reaction conditions may vary with the
32 particular reactants or solvents used, but such conditions
33 can be determined by one skilled in the art by routine
34 optimization procedures.

01 Those skilled in the art will also recognize that it may be
02 necessary to block or protect certain functional groups
03 while conducting the following synthetic procedures. In
04 such cases, the protecting group will serve to protect the
05 functional group from undesired reactions or to block its
06 undesired reaction with other functional groups or with the
07 reagents used to carry out the desired chemical
08 transformations. The proper choice of a protecting group
09 for a particular functional group will be readily apparent
10 to one skilled in the art. Various protecting groups and
11 their introduction and removal are described, for example,
12 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*
13 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,
14 and references cited therein.

15

16 Synthesis

17

18 The polyalkylphenoxyaminoalkanes of the present invention
19 may be prepared by a process which initially involves
20 hydroxyalkylation of a polyalkylphenol of the formula:

21

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26 wherein R is as defined herein, with an alkylene carbonate
27 of the formula:

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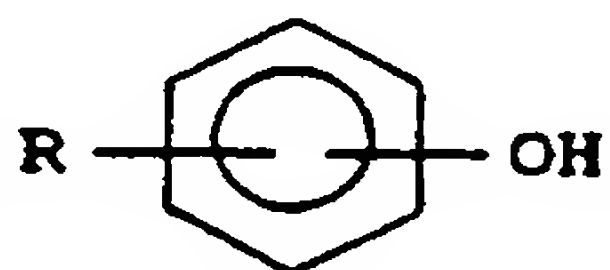
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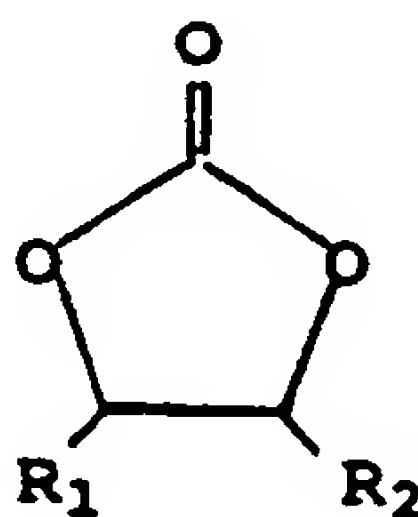
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(II)



(III)

01 wherein R_1 and R_2 are as defined herein, in the presence of
02 a catalytic amount of an alkali metal hydride or hydroxide,
03 or alkali metal salt, to provide a polyalkylphenoxyalkanol
04 of the formula:

05

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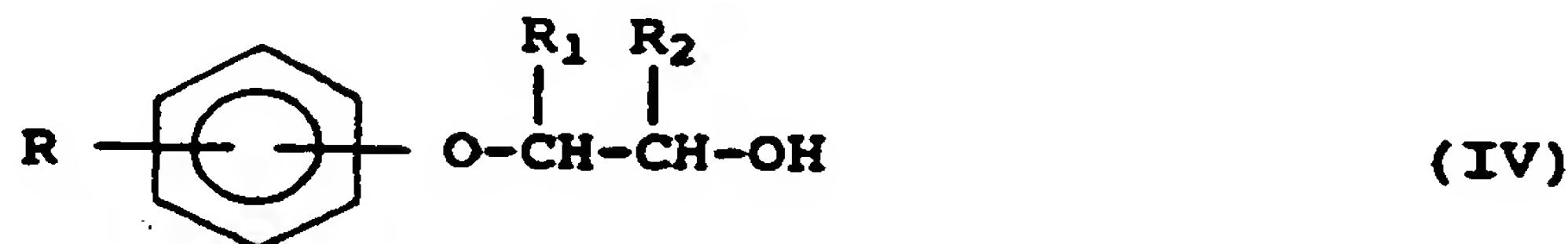
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34



wherein R , R_1 and R_2 are as defined herein.

The polyalkylphenols of formula II are well known materials and are typically prepared by the alkylation of phenol with the desired polyolefin or chlorinated polyolefin. A further discussion of polyalkylphenols can be found, for example, in U.S. Patent No. 4,744,921 and U.S. Patent No. 5,300,701.

Accordingly, the polyalkylphenols of formula II may be prepared from the corresponding olefins by conventional procedures. For example, the polyalkylphenols of formula II above may be prepared by reacting the appropriate olefin or olefin mixture with phenol in the presence of an alkylating catalyst at a temperature of from about 25°C. to 150°C., and preferably 30°C. to 100°C. either neat or in an essentially inert solvent at atmospheric pressure. A preferred alkylating catalyst is boron trifluoride. Molar ratios of reactants may be used. Alternatively, molar excesses of phenol can be employed, i.e., 2 to 3 equivalents of phenol for each equivalent of olefin with unreacted phenol recycled. The latter process maximizes monoalkylphenol. Examples of inert solvents include heptane, benzene, toluene, chlorobenzene and 250 thinner which is a mixture of aromatics, paraffins and naphthenes.

01 The polyalkyl substituent on the polyalkylphenols employed
02 in the invention is generally derived from polyolefins which
03 are polymers or copolymers of mono-olefins, particularly
04 1-mono-olefins, such as ethylene, propylene, butylene, and
05 the like. Preferably, the mono-olefin employed will have 2
06 to about 24 carbon atoms, and more preferably, about 3 to 12
07 carbon atoms. More preferred mono-olefins include
08 propylene, butylene, particularly isobutylene, 1-octene and
09 1-decene. Polyolefins prepared from such mono-olefins
10 include polypropylene, polybutene, especially polyisobutene,
11 and the polyalphaolefins produced from 1-octene and
12 1-decene.

13
14 The preferred polyisobutenes used to prepare the presently
15 employed polyalkylphenols are polyisobutenes which comprise
16 at least about 20% of the more reactive methylvinylidene
17 isomer, preferably at least 50% and more preferably at least
18 70%. Suitable polyisobutenes include those prepared using
19 BF_3 catalysts. The preparation of such polyisobutenes in
20 which the methylvinylidene isomer comprises a high
21 percentage of the total composition is described in U.S.
22 Patent Nos. 4,152,499 and 4,605,808. Such polyisobutenes,
23 known as "reactive" polyisobutenes, yield high molecular
24 weight alcohols in which the hydroxyl group is at or near
25 the end of the hydrocarbon chain. Examples of suitable
26 polyisobutenes having a high alkylvinylidene content include
27 Ultravis 30, a polyisobutene having a number average
28 molecular weight of about 1300 and a methylvinylidene
29 content of about 74%, and Ultravis 10, a polyisobutene
30 having a number average molecular weight of about 950 and a
31 methylvinylidene content of about 76%, both available from
32 British Petroleum.

33

34

01 The alkylene carbonates of formula III are known compounds
02 which are available commercially or can be readily prepared
03 using conventional procedures. Suitable alkylene carbonates
04 include ethylene carbonate, propylene carbonate, 1,2-
05 butylene carbonate, 2,3-butylene carbonate, and the like. A
06 preferred alkylene carbonate is ethylene carbonate.

07
08 The catalyst employed in the reaction of the polyalkylphenol
09 and alkylene carbonate may be any of the well known
10 hydroxyalkylation catalysts. Typical hydroxyalkylation
11 catalysts include alkali metal hydrides, such as lithium
12 hydride, sodium hydride and potassium hydride, alkali metal
13 hydroxides, such as sodium hydroxide and potassium
14 hydroxide, and alkali metal salts, for example, alkali metal
15 halides, such as sodium chloride and potassium chloride, and
16 alkali metal carbonates, such as sodium carbonate and
17 potassium carbonate. The amount of catalyst employed will
18 generally range from about 0.01 to 1.0 equivalent,
19 preferably from about 0.05 to 0.3 equivalent.

20
21 The polyalkylphenol and alkylene carbonate are generally
22 reacted in essentially equivalent amounts in the presence of
23 the hydroxyalkylation catalyst at a temperature in the range
24 of about 100°C. to 210°C., and preferably from about 150°C.
25 to about 170°C. The reaction may take place in the presence
26 or absence of an inert solvent.

27
28 The time of reaction will vary depending on the particular
29 alkylphenol and alkylene carbonate reactants, the catalyst
30 used and the reaction temperature. Generally, the reaction
31 time will range from about two hours to about five hours.
32 The progress of the reaction is typically monitored by the
33 evolution of carbon dioxide. At the completion of the

34

01 reaction, the polyalkylphenoxyalkanol product is isolated
02 using conventional techniques.

03

04 The hydroxyalkylation reaction of phenols with alkylene
05 carbonates is well known in the art and is described, for
06 example, in U.S. Patent Nos. 2,987,555; 2,967,892; 3,283,030
07 and 4,341,905.

08

09 Alternatively, the polyalkylphenoxyalkanol product of
10 formula IV may be prepared by reacting the polyalkylphenol
11 of formula II with an alkylene oxide of the formula:

12

13

14

15



16

17 wherein R₁ and R₂ are as defined herein, in the presence of
18 a hydroxyalkylation catalyst as described above.

19

20 Suitable alkylene oxides of formula V include ethylene
21 oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene
22 oxide, and the like. A preferred alkylene oxide is ethylene
23 oxide.

24

25 In a manner similar to the reaction with alkylene carbonate,
26 the polyalkylphenol and alkylene oxide are reacted in
27 essentially equivalent or equimolar amounts in the presence
28 of 0.01 to 1.0 equivalent of a hydroxyalkylation catalyst,
29 such as sodium or potassium hydride, at a temperature in the
30 range of about 30°C. to about 150°C., for about 2 to about
31 24 hours. The reaction may be conducted in the presence or
32 absence of a substantially anhydrous inert solvent.

33 Suitable solvents include toluene, xylene, and the like.

34 Generally, the reaction is conducted at a pressure

01 sufficient to contain the reactants and any solvent present,
02 typically at atmospheric or higher pressure. Upon
03 completion of the reaction, the polyalkylphenoxyalkanol is
04 isolated by conventional procedures.

05

06 The polyalkylphenoxyalkanol of formula IV is subsequently
07 reacted, either directly or through an intermediate, with an
08 appropriate amine to provide the desired
09 polyalkylphenoxyaminoalkanes of formula I. Suitable amine
10 reactants which may be employed to form the amine component,
11 i.e., substituent A, of the polyalkylphenoxyaminoalkanes of
12 the present invention are discussed more fully below.

13

14 The Amine Component

15

16 In general, the amine component of the present
17 polyalkylphenoxyaminoalkanes will contain an average of at
18 least about one basic nitrogen atom per molecule. A "basic
19 nitrogen atom" is one that is titratable by a strong acid,
20 for example, a primary, secondary, or tertiary amine
21 nitrogen; as distinguished from, for example, an carbamyl
22 nitrogen, e.g., $-\text{OC}(\text{O})\text{NH}-$, which is not titratable with a
23 strong acid. Preferably, at least one of the basic nitrogen
24 atoms of the amine component will be primary or secondary
25 amine nitrogen, more preferably, at least one will be a
26 primary amine nitrogen.

27

28 The amine component of the polyalkylphenoxyaminoalkanes of
29 this invention is preferably derived from ammonia, a primary
30 alkyl or secondary dialkyl monoamine, or a polyamine having
31 a terminal amino nitrogen atom.

32

33 Primary alkyl monoamines useful in preparing compounds of
34 the present invention contain 1 nitrogen atom and from about

01 1 to about 20 carbon atoms, more preferably about 1 to 6
02 carbon atoms, most preferably 1 to 4 carbon atoms. Examples
03 of suitable monoamines include *N*-methylamine, *N*-ethylamine,
04 *N*-*n*-propylamine, *N*-isopropylamine, *N*-*n*-butylamine, *N*-
05 isobutylamine, *N*-sec-butylamine, *N*-tert-butylamine, *N*-*n*-
06 pentylamine, *N*-cyclopentylamine, *N*-*n*-hexylamine, *N*-
07 cyclohexylamine, *N*-octylamine, *N*-decylamine, *N*-dodecylamine,
08 *N*-octadecylamine, *N*-benzylamine, *N*-(2-phenylethyl)amine, 2-
09 aminoethanol, 3-amino-1-propanol, 2-(2-aminoethoxy)ethanol,
10 *N*-(2-methoxyethyl)amine, *N*-(2-ethoxyethyl)amine and the
11 like. Preferred primary amines are *N*-methylamine,
12 *N*-ethylamine and *N*-*n*-propylamine.

13

14 The amine component of the present
15 polyalkylphenoxyaminoalkanes may also be derived from a
16 secondary dialkyl monoamine. The alkyl groups of the
17 secondary amine may be the same or different and will
18 generally each contain about 1 to about 20 carbon atoms,
19 more preferably about 1 to about 6 carbon atoms, most
20 preferably about 1 to about 4 carbon atoms. One or both of
21 the alkyl groups may also contain one or more oxygen atoms.

22

23 Preferably, the alkyl groups of the secondary amine are
24 independently selected from the group consisting of methyl,
25 ethyl, propyl, butyl, pentyl, hexyl, 2-hydroxyethyl and 2-
26 methoxyethyl. More preferably, the alkyl groups are methyl,
27 ethyl or propyl.

28

29 Typical secondary amines which may be used in this invention
30 include *N,N*-dimethylamine, *N,N*-diethylamine, *N,N*-di-*n*-
31 propylamine, *N,N*-diisopropylamine, *N,N*-di-*n*-butylamine,
32 *N,N*-di-sec-butylamine, *N,N*-di-*n*-pentylamine, *N,N*-di-*n*-
33 hexylamine, *N,N*-dicyclohexylamine, *N,N*-dioctylamine,
34 *N*-ethyl-*N*-methylamine, *N*-methyl-*N*-*n*-propylamine, *N*-*n*-butyl-

01 N-methylamine, N-methyl-N-octylamine, N-ethyl-N-
02 isopropylamine, N-ethyl-N-octylamine, N,N-di(2-
03 hydroxyethyl)amine, N,N-di(3-hydroxypropyl)amine,
04 N,N-di(ethoxyethyl)amine, N,N-di(propoxyethyl)amine and the
05 like. Preferred secondary amines are N,N-dimethylamine,
06 N,N-diethylamine and N,N-di-n-propylamine.

07
08 Cyclic secondary amines may also be employed to form the
09 additives of this invention. In such cyclic compounds, the
10 alkyl groups, when taken together, form one or more 5- or
11 6-membered rings containing up to about 20 carbon atoms.
12 The ring containing the amine nitrogen atom is generally
13 saturated, but may be fused to one or more saturated or
14 unsaturated rings. The rings may be substituted with
15 hydrocarbyl groups of from 1 to about 10 carbon atoms and
16 may contain one or more oxygen atoms.

17
18 Suitable cyclic secondary amines include piperidine,
19 4-methylpiperidine, pyrrolidine, morpholine,
20 2,6-dimethylmorpholine and the like.

21
22 Suitable polyamines can have a straight- or branched-chain
23 structure and may be cyclic or acyclic or combinations
24 thereof. Generally, the amine nitrogen atoms of such
25 polyamines will be separated from one another by at least
26 two carbon atoms, i.e., polyamines having an amina
27 structure are not suitable. The polyamine may also contain
28 one or more oxygen atoms, typically present as an ether or a
29 hydroxyl group. Polyamines having a carbon-to-nitrogen ratio
30 of from about 1:1 to about 10:1 are particularly preferred.

31
32 In preparing the compounds of this invention using a
33 polyamine where the various nitrogen atoms of the polyamine
34 are not geometrically equivalent, several substitutional

01 isomers are possible and each of these possible isomers is
02 encompassed within this invention.

03

04 A particularly preferred group of polyamines for use in the
05 present invention are polyalkylene polyamines, including
06 alkylene diamines. Such polyalkylene polyamines will
07 typically contain from about 2 to about 12 nitrogen atoms
08 and from about 2 to about 40 carbon atoms, preferably about
09 2 to 24 carbon atoms. Preferably, the alkylene groups of
10 such polyalkylene polyamines will contain from about 2 to
11 about 6 carbon atoms, more preferably from about 2 to about
12 4 carbon atoms.

13

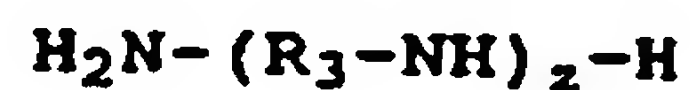
14 Examples of suitable polyalkylene polyamines include
15 ethylenediamine, propylenediamine, isopropylenediamine,
16 butylenediamine, pentylenediamine, hexylenediamine,
17 diethylenetriamine, dipropylenetriamine,
18 dimethylaminopropylamine, diisopropylenetriamine,
19 dibutylenetriamine, di-sec-butylenetriamine,
20 triethylenetetraamine, tripropylenetetraamine,
21 triisobutylenetetraamine, tetraethylenepentamine,
22 pentaethylenhexamine, dimethylaminopropylamine, and
23 mixtures thereof.

24

25 Particularly suitable polyalkylene polyamines are those
26 having the formula:

27

28



29

30 wherein R_3 is a straight- or branched-chain alkylene group
31 having from about 2 to about 6 carbon atoms, preferably from
32 about 2 to about 4 carbon atoms, most preferably about 2
33 carbon atoms, i.e., ethylene ($-\text{CH}_2\text{CH}_2-$); and z is an integer
34 from about 1 to about 4, preferably about 1 or about 2.

01 Particularly preferred polyalkylene polyamines are
02 ethylenediamine, diethylenetriamine, triethylenetetraamine,
03 and tetraethylenepentamine. Most preferred are
04 ethylenediamine and diethylenetriamine, especially
05 ethylenediamine.

06
07 Also contemplated for use in the present invention are
08 cyclic polyamines having one or more 5- to 6-membered rings.
09 Such cyclic polyamines compounds include piperazine,
10 2-methylpiperazine, N-(2-aminoethyl)piperazine,
11 N-(2-hydroxyethyl)piperazine, 1,2-bis-(N-piperazinyl)ethane,
12 3-aminopyrrolidine, N-(2-aminoethyl)pyrrolidine, and the
13 like. Among the cyclic polyamines, the piperazines are
14 preferred.

15
16 Many of the polyamines suitable for use in the present
17 invention are commercially available and others may be
18 prepared by methods which are well known in the art. For
19 example, methods for preparing amines and their reactions
20 are detailed in Sidgewick's "The Organic Chemistry of
21 Nitrogen", Clarendon Press, Oxford, 1966; Noller's
22 "Chemistry of Organic Compounds", Saunders, Philadelphia,
23 2nd Ed., 1957; and Kirk-Othmer's "Encyclopedia of Chemical
24 Technology", 2nd Ed., especially Volume 2, pp. 99-116.

25
26 Preparation of the Polyalkylphenoxyaminoalkane

27
28 As noted above, the polyalkylphenoxyaminoalkanes of the
29 present invention may be conveniently prepared by reacting
30 the polyalkylphenoxyalkanol of formula IV, either directly
31 or through an intermediate, with a nitrogen-containing
32 compound, such as ammonia, a primary or secondary alkyl
33 monoamine, or a polyamine, as described herein.

34

01 Accordingly, the polyalkylphenoxyalkanol of formula IV may
02 be converted to the desired polyalkylphenoxyaminoalkane by a
03 variety of procedures known in the art.

04

05 For example, the terminal hydroxy group on the
06 polyalkylphenoxyalkanol may first be converted to a suitable
07 leaving group, such as a mesylate, chloride or bromide, and
08 the like, by reaction with a suitable reagent, such as
09 methanesulfonyl chloride. The resulting

10 polyalkylphenoxyalkyl mesylate or equivalent intermediate
11 may then be converted to a phthalimide derivative by
12 reaction with potassium phthalimide in the presence of a
13 suitable solvent, such as *N,N*-dimethylformamide. The
14 polyalkylphenoxyalkyl phthalimide derivative is subsequently
15 converted to the desired polyalkylphenoxyaminoalkane by
16 reaction with a suitable amine, such as hydrazine.

17 Alternatively, the leaving group can be converted to an
18 azide, as described, for example, in Turnbull Scriven,
19 Chemical Reviews, Volume 88, pages 297-368, 1988. The azide
20 is subsequently converted to the desired
21 polyalkylphenoxyaminoalkane by reduction with hydrogen and a
22 catalyst, such as palladium on carbon or a Lindlar catalyst.

23

24 The polyalkylphenoxyalkanol of formula IV may also be
25 converted to the corresponding polyalkylphenoxyalkyl
26 chloride by reaction with a suitable halogenating agent,
27 such as HCl, thionyl chloride, or epichlorohydrin, followed
28 by displacement of the chloride with a suitable amine, such
29 as ammonia, a primary or secondary alkyl monoamine, or a
30 polyamine, as described, for example, in U.S. Patent No.
31 4,247,301 to Honnen, the disclosure of which is incorporated
32 herein by reference.

33

34

01 Alternatively, the polyalkylphenoxyaminoalkanes of the
02 present invention may be prepared from the corresponding
03 polyalkylphenoxyalkanol by a process commonly referred to as
04 reductive amination, such as described in U.S. Patent No.
05 5,112,364 to Rath et al. and U.S. Patent No. 4,332,595 to
06 Herbstman et al., the disclosures of which are incorporated
07 herein by reference.

08

09 In the reductive amination procedure, the
10 polyalkylphenoxyalkanol is aminated with an appropriate
11 amine, such as ammonia or a primary alkyl monoamine, in the
12 presence of hydrogen and a hydrogenation-dehydrogenation
13 catalyst. The amination reaction is typically carried out
14 at temperatures in the range of about 160°C to about 250°C
15 and pressures of about 1,000 to about 5,000 psig, preferably
16 about 1,500 to about 3,000 psig. Suitable hydrogenation-
17 dehydrogenation catalysts include those containing platinum,
18 palladium, cobalt, nickel, copper, or chromium, or mixtures
19 thereof. Generally, an excess of the ammonia or amine
20 reactant is used, such as about a 5-fold to about 60-fold
21 molar excess, and preferably about a 10-fold to about 40-
22 fold molar excess, of ammonia or amine.

23

24 When the reductive amination is carried out with a polyamine
25 reactant, the amination is preferably conducted using a two-
26 step procedure as described in commonly-assigned copending
27 U.S. Patent application Serial No. 08/574,485, filed
28 December 19, 1995, and titled, "Reductive Amination Process
29 for Manufacturing a Fuel Additive From Polyoxybutylene
30 Alcohol with Ethylene Diamine", the disclosure of which is
31 incorporated herein by reference in its entirety. According
32 to this procedure, an appropriate alcohol is first contacted
33 with a hydrogenation-dehydrogenation catalyst at a
34 temperature of at least 230°C to provide a carbonyl-

01 containing intermediate, which is subsequently reacted with
02 a polyamine at a temperature below about 190°C in the
03 presence of hydrogen and a hydrogenation catalyst to produce
04 the desired polyamine adduct.

05

06 In an alternative procedure for preparing the
07 polyalkylphenoxyaminoalkanes of the present invention, the
08 polyalkylphenol of formula II may be reacted with an
09 aziridine of the formula:

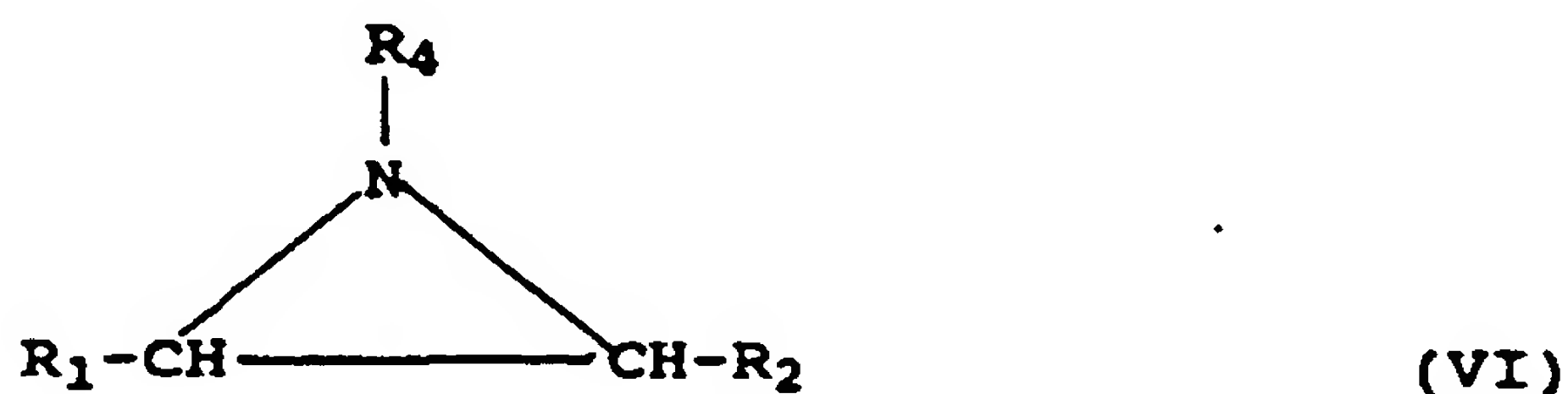
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15

16 wherein R_1 and R_2 are as defined herein, and R_4 is hydrogen
17 or alkyl of 1 to 20 carbon atoms. A preferred aziridine is
18 one wherein R_1 is hydrogen, R_2 is hydrogen, methyl or ethyl,
19 and R_4 is hydrogen.

20

21 The reaction of aziridines with alcohols to produce beta-
22 amino ethers is well known in the art and is discussed, for
23 example, in Ham and Dermer, "Ethyleneimine and Other
24 Aziridines", Academic Press, New York, 1969, pages 224-227
25 and 256-257.

26

27

Fuel Compositions

28

29 The compounds of the present invention are useful as
30 additives in hydrocarbon fuels to prevent and control engine
31 deposits, particularly intake valve deposits. The proper
32 concentration of additive necessary to achieve the desired
33 deposit control varies depending upon the type of fuel

34

01 employed, the type of engine, and the presence of other fuel
02 additives.

03

04 In general, the concentration of the compounds of this
05 invention in hydrocarbon fuel will range from about 50 to
06 about 2500 parts per million (ppm) by weight, preferably
07 from 75 to 1,000 ppm. When other deposit control additives
08 are present, a lesser amount of the present additive may be
09 used.

10

11 The compounds of the present invention may be formulated as
12 a concentrate using an inert stable oleophilic (i.e.,
13 dissolves in gasoline) organic solvent boiling in the range
14 of about 150°F. to 400°F. (about 65°C. to 205°C.).

15 Preferably, an aliphatic or an aromatic hydrocarbon solvent
16 is used, such as benzene, toluene, xylene or higher-boiling
17 aromatics or aromatic thinners. Aliphatic alcohols
18 containing about 3 to 8 carbon atoms, such as isopropanol,
19 isobutylcarbinol, n-butanol and the like, in combination
20 with hydrocarbon solvents are also suitable for use with the
21 present additives. In the concentrate, the amount of the
22 additive will generally range from about 10 to about
23 70 weight percent, preferably 10 to 50 weight percent, more
24 preferably from 20 to 40 weight percent.

25 In gasoline fuels, other fuel additives may be employed with
26 the additives of the present invention, including, for
27 example, oxygenates, such as t-butyl methyl ether, antiknock
28 agents, such as methylcyclopentadienyl manganese
29 tricarbonyl, and other dispersants/detergents, such as
30 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines,
31 hydrocarbyl poly(oxyalkylene) aminocarbamates, or
32 succinimides. Additionally, antioxidants, metal
33 deactivators and demulsifiers may be present.

34

01 In diesel fuels, other well-known additives can be employed,
02 such as pour point depressants, flow improvers, cetane
03 improvers, and the like.

04

05 A fuel-soluble, nonvolatile carrier fluid or oil may also be
06 used with the compounds of this invention. The carrier
07 fluid is a chemically inert hydrocarbon-soluble liquid
08 vehicle which substantially increases the nonvolatile
09 residue (NVR), or solvent-free liquid fraction of the fuel
10 additive composition while not overwhelmingly contributing
11 to octane requirement increase. The carrier fluid may be a
12 natural or synthetic oil, such as mineral oil, refined
13 petroleum oils, synthetic polyalkanes and alkenes, including
14 hydrogenated and unhydrogenated polyalphaolefins, and
15 synthetic polyoxyalkylene-derived oils, such as those
16 described, for example, in U.S. Patent No. 4,191,537 to
17 Lewis, and polyesters, such as those described, for example,
18 in U.S. Patent Nos. 3,756,793 to Robinson and 5,004,478 to
19 Vogel et al., and in European Patent Application
20 Nos. 356,726, published March 7, 1990, and 382,159,
21 published August 16, 1990.

22

23 These carrier fluids are believed to act as a carrier for
24 the fuel additives of the present invention and to assist in
25 removing and retarding deposits. The carrier fluid may also
26 exhibit synergistic deposit control properties when used in
27 combination with a compound of this invention.

28

29 The carrier fluids are typically employed in amounts ranging
30 from about 100 to about 5000 ppm by weight of the
31 hydrocarbon fuel, preferably from 400 to 3000 ppm of the
32 fuel. Preferably, the ratio of carrier fluid to deposit
33 control additive will range from about 0.5:1 to about 10:1,
34 more preferably from 1:1 to 4:1, most preferably about 2:1.

01 When employed in a fuel concentrate, carrier fluids will
02 generally be present in amounts ranging from about 20 to
03 about 60 weight percent, preferably from 30 to 50 weight
04 percent.

05

06

PREPARATIONS AND EXAMPLES

07

08 A further understanding of the invention can be had in the
09 following nonlimiting Examples. Wherein unless expressly
10 stated to the contrary, all temperatures and temperature
11 ranges refer to the Centigrade system and the term "ambient"
12 or "room temperature" refers to about 20°C.-25°C. The term
13 "percent" or "%" refers to weight percent and the term
14 "mole" or "moles" refers to gram moles. The term
15 "equivalent" refers to a quantity of reagent equal in moles,
16 to the moles of the preceding or succeeding reactant recited
17 in that example in terms of finite moles or finite weight or
18 volume. Where given, proton-magnetic resonance spectrum
19 (p.m.r. or n.m.r.) were determined at 300 MHz, signals are
20 assigned as singlets (s), broad singlets (bs), doublets (d),
21 double doublets (dd), triplets (t), double triplets (dt),
22 quartets (q), and multiplets (m), and cps refers to cycles
23 per second.

24

25

Example 1

26

27

Preparation of Polyisobutyl Phenol

28

29 To a flask equipped with a magnetic stirrer, reflux
30 condenser, thermometer, addition funnel and nitrogen inlet
31 was added 203.2 grams of phenol. The phenol was warmed to
32 40°C. and the heat source was removed. Then, 73.5

33

34

01 milliliters of boron trifluoride etherate was added
02 dropwise. 1040 grams of Ultravis 10 Polyisobutene
03 (molecular weight 950, 76% methylvinylidene, available from
04 British Petroleum) was dissolved in 1,863 milliliters of
05 hexane. The polyisobutene was added to the reaction at a
06 rate to maintain the temperature between 22°C-27°C. The
07 reaction mixture was stirred for 16 hours at room
08 temperature. Then, 400 milliliters of concentrated ammonium
09 hydroxide was added, followed by 2,000 milliliters of
10 hexane. The reaction mixture was washed with water (3 X
11 2,000 milliliters), dried over magnesium sulfate, filtered
12 and the solvents removed under vacuum to yield 1,056.5 grams
13 of a crude reaction product. The crude reaction product was
14 determined to contain 80% of the desired product by proton
15 NMR and chromatography on silica gel eluting with hexane,
16 followed by hexane: ethylacetate: ethanol (93:5:2).

17

18

Example 2

19

20

Preparation of

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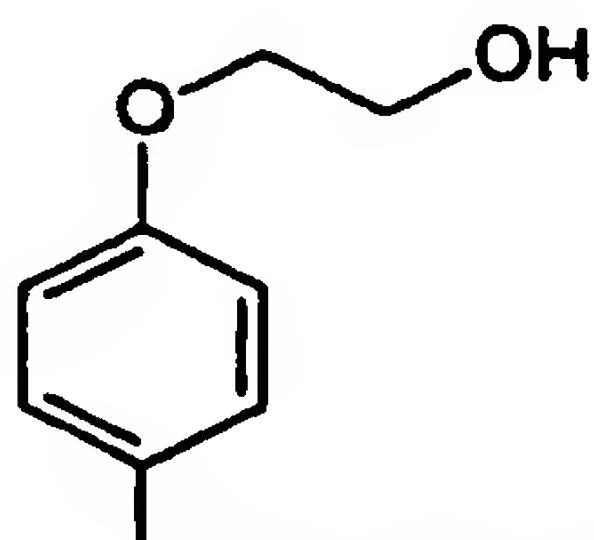
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28

PIB (molecular weight ~ 950)

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34

Potassium hydride (1.1 grams of a 35 weight percent dispersion of in mineral oil) and 4- polyisobutyl phenol (99.7 grams, prepared as in Example 1) were added to a flask equipped with a magnetic stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at

-27-

01 130°C for one hour and then cooled to 100°C. Ethylene
02 carbonate (8.6 grams) was added and the mixture was heated
03 at 160°C for 16 hours. The reaction was cooled to room
04 temperature and one milliliter of isopropanol was added.
05 The reaction was diluted with one liter of hexane, washed
06 three times with water and once with brine. The organic
07 layer was dried over anhydrous magnesium sulfate, filtered
08 and the solvents removed in vacuo to yield 98.0 grams of the
09 desired product as a yellow oil.

10

11

Example 3

12

13

Preparation of

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15

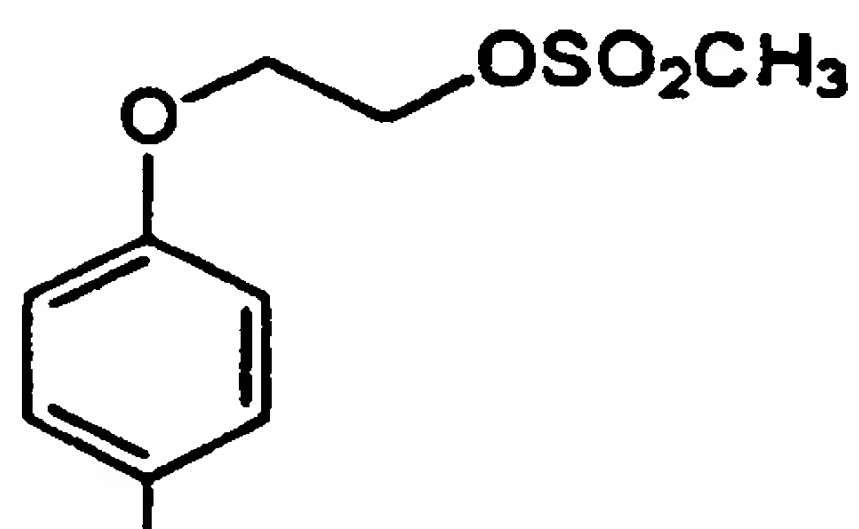
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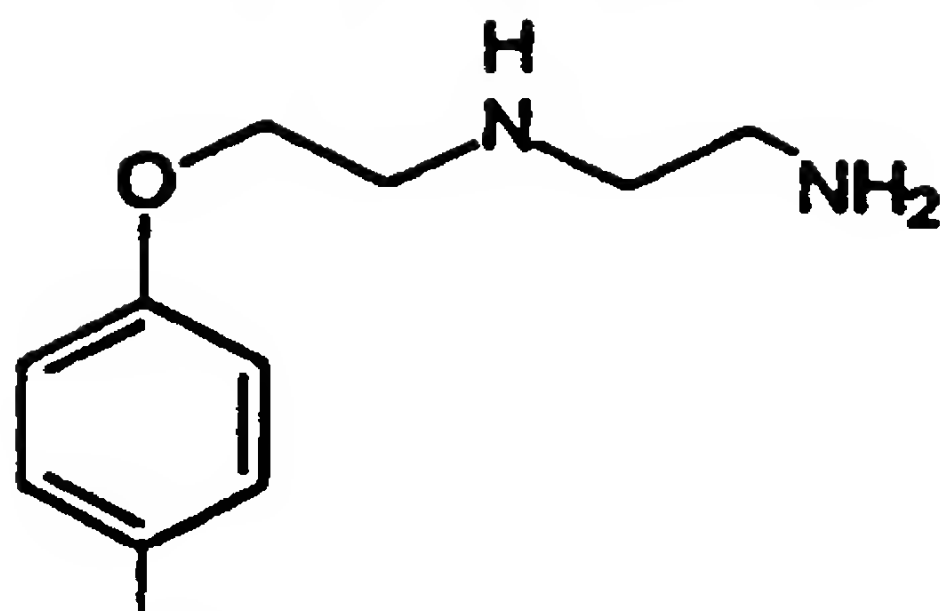
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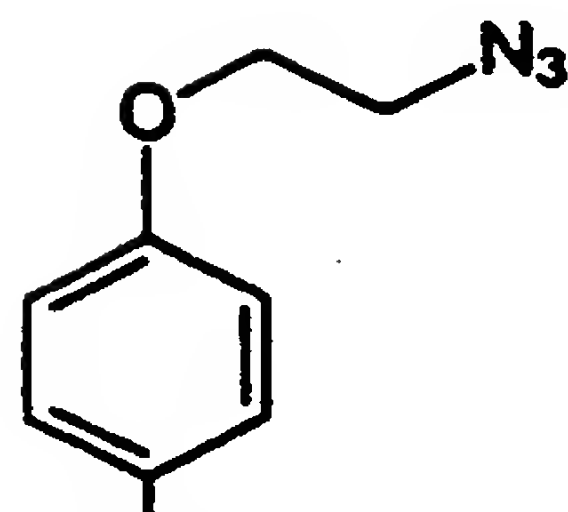
34

The alcohol from Example 2 (20.0 grams), triethylamine (2.9 mL), and anhydrous dichloromethane (200 mL) were combined. The solution was cooled to 0°C and methanesulfonyl chloride (1.5 mL) was added dropwise. The reaction was stirred at room temperature under nitrogen for 16 hours. The solution was diluted with dichloromethane (600 mL) and was washed twice with saturated aqueous sodium bicarbonate solution and once with brine. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvents removed in vacuo to yield 20.4 grams as a yellow oil.

Example 4Preparation of

PB (molecular weight ~ 950)

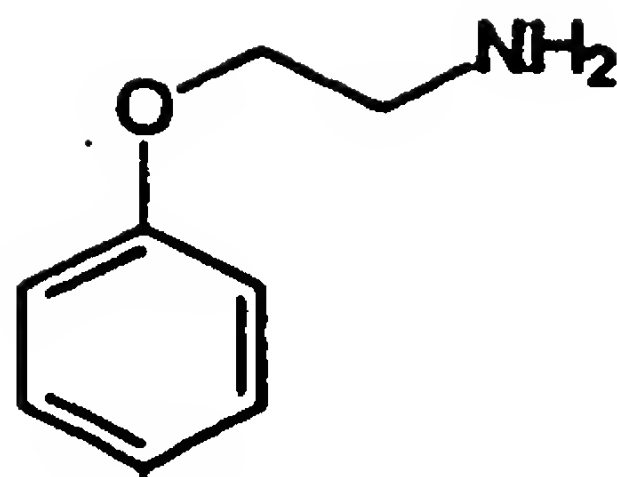
Ethylenediamine (12.3 mL) and anhydrous toluene (100 mL) were combined under nitrogen. The product from Example 3 (20.4 grams, dissolved in 100 mL of anhydrous toluene) was added dropwise. The resulting solution was refluxed for 16 hours. The solution was diluted with hexane (600 mL) and was washed once with saturated aqueous sodium bicarbonate solution, three times with water and once with brine. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvents removed in vacuo to yield 15.1 grams as a yellow oil. The oil was chromatographed on silica gel, eluting with hexane / diethyl ether (50:50) then hexane / diethyl ether / methanol / isopropylamine (40:40:15:5) to yield 10.3 grams of the desired product as a yellow oil. ¹H NMR (CDCl₃) δ 7.25 (d, 2H), 6.8 (d, 2H), 4.1 (t, 2H), 3.0 (t, 2H), 2.85 (t, 2H), 2.75 (t, 2H), 1.95 (bs, 3H), 1.5-0.7 (m, 137H).

Example 5Preparation of

PIB (molecular weight ~ 950)

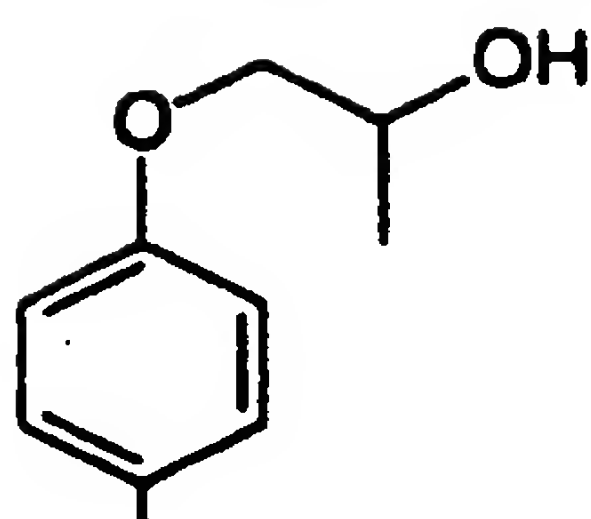
A mesylate prepared as described in Example 3 (406.5 grams), sodium azide (198.2 grams), Adogen 464, a methyltrialkyl (C₈-C₁₀) ammonium chloride available from Ashland Chemical (8.0 mL), N,N - dimethylformamide (800 mL) and toluene (1.2 L) were combined. The reaction was refluxed for sixteen hours and cooled to room temperature. The mixture was filtered and the solvent was removed in vacuo. The residue was diluted with hexane (3.0 L) and washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 334.3 grams of the desired azide as a yellow oil.

-30-

Example 6Preparation of

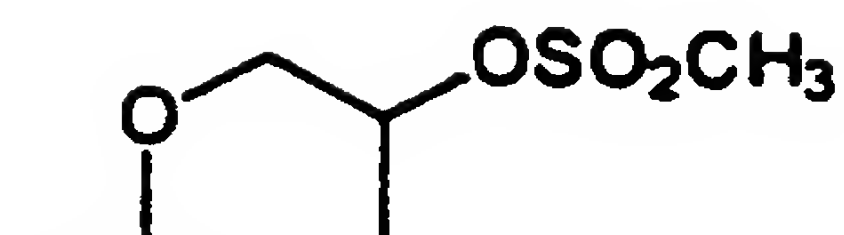
PB (molecular weight ~ 950)

A solution of the product from Example 5 (334.3 grams) in ethyl acetate (750 mL) and toluene (750 mL), containing 10% palladium on charcoal (7.0 grams) was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yielded 322.3 grams of the desired product as a yellow oil. ¹H NMR (CDCl₃) δ 7.25 (d, 2H), 6.8 (d, 2H), 4.0 (t, 1H), 3.1 (t, 2H), 2.35 (bs, 2H), 0.7-1.6 (m, 137H).

Example 7Preparation of

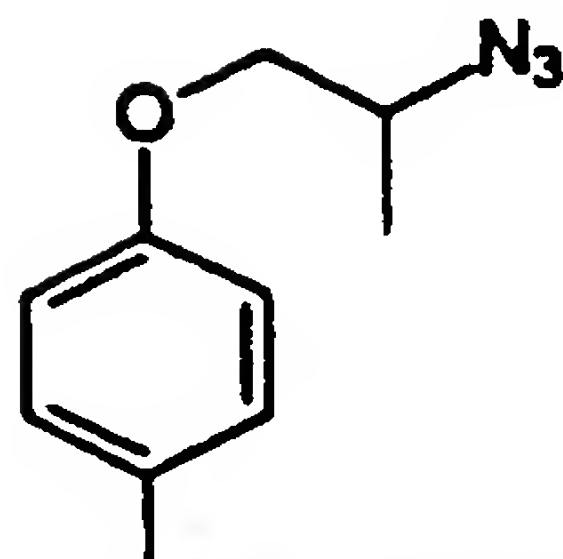
PIB (molecular weight ~ 950)

Potassium hydride (15.1 grams of a 35 weight percent dispersion of in mineral oil) and 4- polyisobutyl phenol (1378.5 grams, prepared as in Example 1) were added to a flask equipped with a mechanical stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Propylene carbonate (115.7 milliliters) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and ten milliliters of isopropanol were added. The reaction was diluted with ten liters of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 1301.7 grams of the desired product as a yellow oil.

Example 8Preparation of

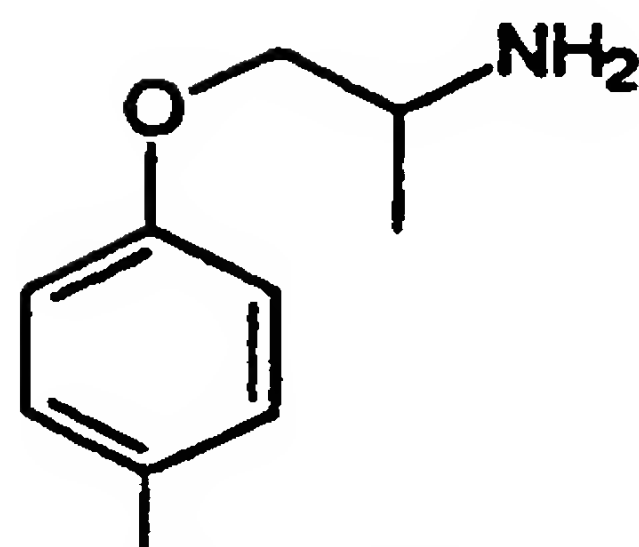
PB (molecular weight ~ 950)

The alcohol from Example 7 (50.0 grams), triethylamine (7.0 mL), and anhydrous dichloromethane (500 mL) were combined. The solution was cooled to 0°C and methanesulfonyl chloride (3.7 mL) was added dropwise. The reaction was stirred at room temperature under nitrogen for 16 hours. The solution was diluted with dichloromethane (1.5L) and was washed three times with saturated aqueous sodium bicarbonate solution and once with brine. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvents removed in vacuo to yield 57.7 grams as a yellow oil.

Example 9Preparation of

PIB (molecular weight ~ 950)

The mesylate from Example 8 (57.7 grams), sodium azide (27.1 grams), Adogen 464 (1.0 mL), N,N - dimethylformamide (400 mL) and toluene (600 mL) were combined. The reaction was refluxed for sixteen hours and cooled to room temperature. The mixture was filtered and the solvent was removed in vacuo . The residue was diluted with hexane (1.5 L) and washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 43.1 grams of the desired azide as a yellow oil.

Example 10Preparation of

PIB (molecular weight ~ 950)

A solution of the product from Example 9 (43.1 grams) in ethyl acetate (100 mL) and toluene (100 mL), containing 10% palladium on charcoal (2.0 grams) was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yielded 41.5 grams of the desired product as a yellow oil. ¹H NMR (CDCl₃) δ 7.25 (d, 2H), 6.85 (d, 2H), 3.9 (abq, 1H), 3.65 (abq, 1H), 3.35 (m, 1H), 1.9 (bs, 2H), 0.7-1.6 (m, 140H).

Example 11Single-Cylinder Engine Test

The test compounds were blended in gasoline and their deposit reducing capacity determined in an ASTM/CFR single-cylinder engine test.

A Waukesha CFR single-cylinder engine was used. Each run was carried out for 15 hours, at the end of which time the intake valve was removed, washed with hexane and weighed.

01 The previously determined weight of the clean valve was
02 subtracted from the weight of the valve at the end of the
03 run. The differences between the two weights is the weight
04 of the deposit. A lesser amount of deposit indicates a
05 superior additive. The operating conditions of the test
06 were as follows: water jacket temperature 200°F; vacuum of
07 12 in Hg, air-fuel ratio of 12, ignition spark timing of
08 400 BTC; engine speed is 1800 rpm; the crankcase oil is a
09 commercial 30W oil.

10
11 The amount of carbonaceous deposit in milligrams on the
12 intake valves is reported for each of the test compounds in
13 Table I and Table II.

14 TABLE I

15
16 Intake Valve Deposit Weight
17 (in milligrams)

18 Sample ¹	Run 1	Run 2	Average
19 Base Fuel	333.5	354.9	344.2
20 Example 4	22.5	22.7	22.6

21
22
23 ¹At 150 parts per million actives (ppma).

24
25 TABLE II

26
27 Intake Valve Deposit Weight
28 (in milligrams)

29 Sample ¹	Run 1	Run 2	Average
30 Base Fuel	323.8	312.1	318.0
31 Example 6	12.1	21.0	16.6

32
33 ¹At 125 parts per million actives (ppma).

34

01 The base fuel employed in the above single-cylinder engine
02 tests was a regular octane unleaded gasoline containing no
03 fuel detergent. The test compounds were admixed with the
04 base fuel to give the concentrations indicated in the
05 tables.

06

07 The data in Table I and Table II illustrates the significant
08 reduction in intake valve deposits provided by the
09 polyalkylphenoxylaminoalkanes of the present invention
10 (Examples 4 and 6) compared to the base fuel.

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01 WHAT IS CLAIMED IS:

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03 1. A compound of the formula:

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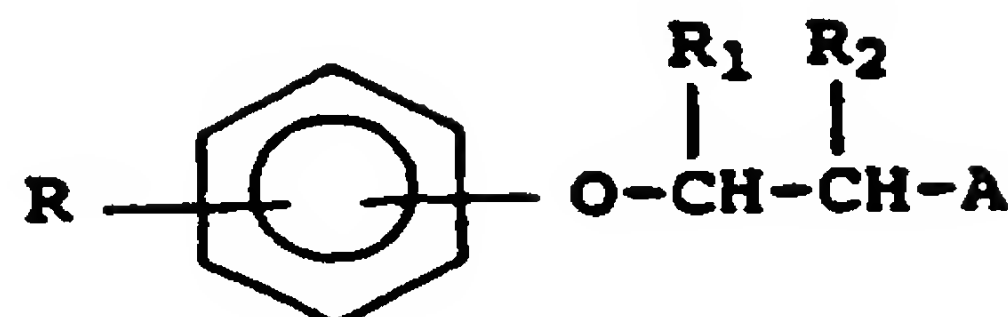
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or a fuel-soluble salt thereof, wherein R is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000;

R₁ and R₂ are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

A is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms.

2. The compound according to Claim 1, wherein one of R₁ and R₂ is hydrogen or lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen.

3. The compound according to Claim 2, wherein one of R₁ and R₂ is hydrogen, methyl or ethyl, and the other is hydrogen.

4. The compound according to Claim 3, wherein R₂ is hydrogen, methyl or ethyl, and R₁ is hydrogen.

- 01 5. The compound according to Claim 1, wherein R is a
02 polyalkyl group having an average molecular weight in
03 the range of about 600 to 3,000.
- 04 6. The compound according to Claim 5, wherein R is a
05 polyalkyl group having an average molecular weight in
06 the range of about 700 to 3,000.
- 07
- 08 7. The compound according to Claim 6, wherein R is a
09 polyalkyl group having an average molecular weight in
10 the range of about 900 to 2,500.
- 11
- 12 8. The compound according to Claim 1, wherein R is a
13 polyalkyl group derived from polypropylene, polybutene,
14 or a polyalphaolefin oligomer of 1-octene or 1-decene.
- 15
- 16 9. The compound according to Claim 8, wherein R is a
17 polyalkyl group derived from polyisobutene.
- 18
- 19 10. The compound according to Claim 9, wherein the
20 polyisobutene contains at least about 20% of a
21 methylvinylidene isomer.
- 22
- 23 11. The compound according to Claim 1, wherein A is amino,
24 N-alkyl amino or a polyamine moiety.
- 25
- 26 12. The compound according to Claim 11, wherein A is amino
27 or N-alkyl amino having from about 1 to about 4 carbon
atoms in the alkyl group.
- 28
- 29 13. The compound according to Claim 12, wherein A is amino.
- 30
- 31 14. The compound according to Claim 11, wherein A is a
32 polyamine moiety having from about 2 to about 12 amine
33 nitrogen atoms and from about 2 to about 40 carbon
34 atoms.

01 15. The compound according to Claim 14, wherein A is a
02 polyamine moiety derived from a polyalkylene polyamine
03 containing from about 2 to about 12 amine nitrogen
04 polyamine atoms and from about 2 to about 24 carbon
05 atoms.

06 16. The compound according to Claim 15, wherein the
07 polyalkylene polyamine has the formula:
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13 wherein R_3 is an alkylene group having from about 2 to
14 about 6 carbon atoms and z is an integer from about 1
15 to about 4.
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17 17. The compound according to Claim 16, wherein R_3 is an
18 alkylene group having from about 2 to about 4 carbon
19 atoms.
20

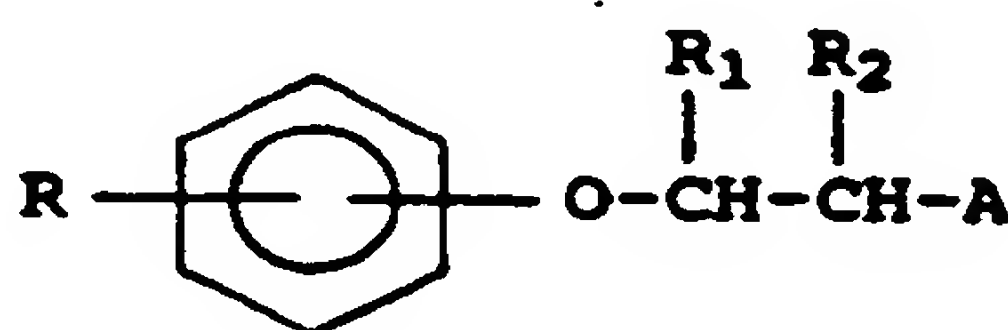
21 18. The compound according to Claim 17, wherein the
22 polyalkylene polyamine is ethylene diamine or
23 diethylene triamine.
24

25 19. The compound according to Claim 18, wherein the
26 polyalkylene polyamine is ethylene diamine.
27

28 20. The compound according to Claim 1, wherein R is a
29 polyalkyl group derived from polyisobutene, R_1 and R_2
30 are hydrogen and A is amino or a polyamine moiety
31 derived from ethylene diamine.

32 21. A fuel composition comprising a major amount of
33 hydrocarbons boiling in the gasoline or diesel range
34

01 and an effective deposit-controlling amount of a
02 compound of the formula:



10 or a fuel-soluble salt thereof, wherein R is a
11 polyalkyl group having an average molecular weight in
12 the range of about 600 to 5,000;

13 R₁ and R₂ are independently hydrogen or lower alkyl
14 having 1 to 6 carbon atoms; and

15
16 A is amino, N-alkyl amino having about 1 to about 20
17 carbon atoms in the alkyl group, N,N-dialkyl amino
18 having about 1 to about 20 carbon atoms in each alkyl
19 group, or a polyamine moiety having about 2 to about 12
20 amine nitrogen atoms and about 2 to about 40 carbon
21 atoms.

22
23 22. The fuel composition according to Claim 21, wherein one
24 of R₁ and R₂ is hydrogen or lower alkyl of 1 to 4
25 carbon atoms, and the other is hydrogen.

26
27 23. The fuel composition according to Claim 22, wherein one
28 of R₁ and R₂ is hydrogen, methyl or ethyl, and the
29 other is hydrogen.

30 24. The fuel composition according to Claim 23, wherein R₂
31 is hydrogen, methyl or ethyl, and R₁ is hydrogen.
32
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- 01 25. The fuel composition according to Claim 21, wherein R
02 is a polyalkyl group having an average molecular weight
03 in the range of about 600 to 3,000.
- 04 26. The fuel composition according to Claim 25, wherein R
05 is a polyalkyl group having an average molecular weight
06 in the range of about 700 to 3,000.
- 07
08 27. The fuel composition according to Claim 26, wherein R₁
09 is a polyalkyl group having an average molecular weight
10 in the range of about 900 to 2,500.
- 11
12 28. The fuel composition according to Claim 21, wherein R
13 is a polyalkyl group derived from polypropylene,
14 polybutene, or a polyalphaolefin oligomer of 1-octene
15 or 1-decene.
- 16 29. The fuel composition according to Claim 28, wherein R
17 is a polyalkyl group derived from polyisobutene.
- 18
19 30. The fuel composition according to Claim 29, wherein the
20 polyisobutene contains at least about 20% of a
21 methylvinylidene isomer.
- 22
23 31. The fuel composition according to Claim 21, wherein A
24 is amino, N-alkyl amino or a polyamine moiety.
- 25 32. The fuel composition according to Claim 31, wherein A
26 is amino or N-alkyl amino having from about 1 to about
27 4 carbon atoms in the alkyl group.
- 28
29 33. The fuel composition according to Claim 32, wherein A
30 is amino.
- 31
32 34. The fuel composition according to Claim 31, wherein A
33 is a polyamine moiety having from about 2 to about 12
34

01 amine nitrogen atoms and from about 2 to about 40
02 carbon atoms.

03 35. The fuel composition according to Claim 34, wherein A
04 is a polyamine moiety derived from a polyalkylene
05 polyamine containing from about 2 to about 12 amine
06 nitrogen polyamine atoms and from about 2 to about 24
07 carbon atoms.
08

09 36. The fuel composition according to Claim 35, wherein the
10 polyalkylene polyamine has the formula:
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16 wherein R_3 is an alkylene group having from about 2 to
17 about 6 carbon atoms and z is an integer from about 1
18 to about 4.
19

20 37. The fuel composition according to Claim 36, wherein R_3
21 is an alkylene group having from about 2 to about 4
22 carbon atoms.
23

24 38. The fuel composition according to Claim 37, wherein the
25 polyalkylene polyamine is ethylene diamine or
26 diethylene triamine.
27

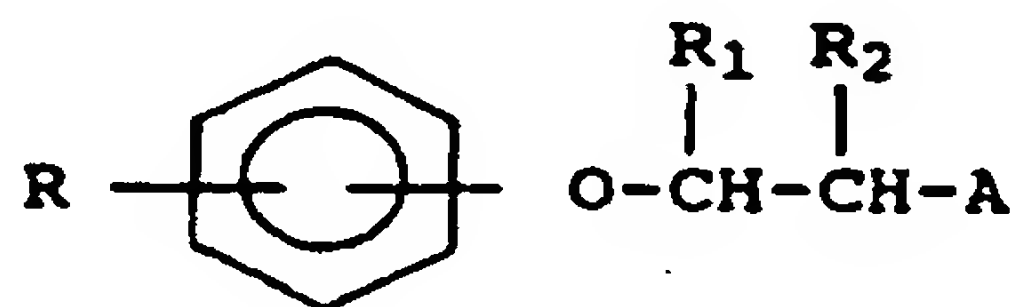
28 39. The fuel composition according to Claim 38, wherein the
29 polyalkylene polyamine is ethylene diamine.
30

31 40. The fuel composition according to Claim 21, wherein R
32 is a polyalkyl group derived from polyisobutene, R_1 and
33 R_2 are hydrogen and A is amino or a polyamine moiety
34 derived from ethylene diamine.

01 41. The fuel composition according to Claim 21, wherein the
02 composition contains from about 50 to about 2,000 parts
03 per million by weight of said compound.

04 42. The fuel composition according to Claim 21, where the
05 composition further contains from about 100 to about
06 5,000 parts per million by weight of a fuel-soluble,
07 nonvolatile carrier fluid.
08

09 43. A fuel concentrate comprising an inert stable
10 oleophilic organic solvent boiling in the range of from
11 about 150°F. to 400°F. and from about 10 to about 70
12 weight percent of a compound of the formula:
13



20 or a fuel-soluble salt thereof, wherein R is a
21 polyalkyl group having an average molecular weight in
22 the range of about 600 to 5,000;

23 R₁ and R₂ are independently hydrogen or lower alkyl
24 having 1 to 6 carbon atoms; and
25

26 A is amino, N-alkyl amino having about 1 to about 20
27 carbon atoms in the alkyl group, N,N-dialkyl amino
28 having about 1 to about 20 carbon atoms in each alkyl
29 group, or a polyamine moiety having about 2 to about 12
30 amine nitrogen atoms and about 2 to about 40 carbon
31 atoms.
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- 01 44. The fuel concentrate according to Claim 43, wherein one
02 of R_1 and R_2 is hydrogen or lower alkyl of 1 to 4
03 carbon atoms, and the other is hydrogen.
04
- 05 45. The fuel concentrate according to Claim 44, wherein one
06 of R_1 and R_2 is hydrogen, methyl or ethyl, and the
07 other is hydrogen.
08
- 09 46. The fuel concentrate according to Claim 45, wherein R_2
10 is hydrogen, methyl or ethyl, and R_1 is hydrogen.
11
- 12 47. The fuel concentrate according to Claim 43, wherein R
13 is a polyalkyl group having an average molecular weight
14 in the range of about 600 to 3,000.
15
- 16 48. The fuel concentrate according to Claim 47, wherein R
17 is a polyalkyl group having an average molecular weight
18 in the range of about 700 to 3,000.
19
- 20 49. The fuel concentrate according to Claim 48, wherein R
21 is a polyalkyl group having an average molecular weight
22 in the range of about 900 to 2,500.
23
- 24 50. The fuel concentrate according to Claim 43, wherein R
25 is a polyalkyl group derived from polypropylene,
26 polybutene, or a polyalphaolefin oligomer of 1-octene
27 or 1-decene.
28
- 29 51. The fuel concentrate according to Claim 50, wherein R
30 is a polyalkyl group derived from polyisobutene.
31
- 32 52. The fuel concentrate according to Claim 51, wherein the
33 polyisobutene contains at least about 20% of a
34 methylvinylidene isomer.

- 01 53. The fuel concentrate according to Claim 43, wherein A
02 is amino, N-alkyl amino or a polyamine moiety.
- 03 54. The fuel concentrate according to Claim 53, wherein A
04 is amino or N-alkyl amino having from about 1 to about
05 4 carbon atoms in the alkyl group.
- 06
07 55. The fuel concentrate according to Claim 54, wherein A
08 is amino.
- 09
10 56. The fuel composition according to Claim 53, wherein A
11 is a polyamine moiety having from about 2 to about 12
12 amine nitrogen atoms and from about 2 to about 40
13 carbon atoms.
- 14 57. The fuel concentrate according to Claim 56, wherein A
15 is a polyamine moiety derived from a polyalkylene
16 polyamine containing from about 2 to about 12 amine
17 nitrogen polyamine atoms and from about 2 to about 24
18 carbon atoms.
- 19
20 58. The fuel concentrate according to Claim 57, wherein the
21 polyalkylene polyamine has the formula:
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23
24
$$\text{H}_2\text{N}-(\text{R}_3-\text{NH})_z-\text{H}$$

25
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27 wherein R_3 is an alkylene group having from about 2 to
28 about 6 carbon atoms and z is an integer from about 1
29 to about 4.
- 30
31 59. The fuel concentrate according to Claim 58, wherein R_3
32 is an alkylene group having from about 2 to about 4
33 carbon atoms.
- 34

- 01 60. The fuel concentrate according to Claim 59, wherein the
02 polyalkylene polyamine is ethylene diamine or
03 diethylene triamine.
04
- 05 61. The fuel concentrate according to Claim 60, wherein the
06 polyalkylene polyamine is ethylene diamine.
07
- 08 62. The fuel concentrate according to Claim 43, wherein R
09 is a polyalkyl group derived from polyisobutene, R₁ and
10 R₂ are hydrogen and A is amino or a polyamine moiety
11 derived from ethylene diamine.
- 12 63. The fuel concentrate according to Claim 43, wherein the
13 fuel concentrate further contains from about 20 to
14 about 60 weight percent of a fuel-soluble, nonvolatile
15 carrier fluid.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07991

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10L 1/22; C07C 217/64

US CL : 044/424, 425; 564/353, 354

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 044/424, 425; 564/353, 354

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
noneElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,778,481 A (COURTNEY) 18 October 1988, column 5, lines 39 to column 6, line 49.	1-63
A	US 4,568,354 A (DAVIS ET AL) 04 February 1986, column 2, lines 5-24.	1-63
A	US 4,392,866 A (SUNG ET AL) 12 July 1983, column 1, lines 26-47.	1-63
A	US 4,259,086 A (MACHLEDER ET AL) 31 March 1981, column 17, lines 57 to column 18, line 2.	1-63
A	US 4,147,641 A (MACHLEDER ET AL) 03 April 1979, column 2, lines 29-64.	1-63
A	US 3,849,083 A (DUBECK) 19 November 1974, column 1, lines 28-37.	1-63

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

A	document defining the general state of the art which is not considered to be of particular relevance	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E	earlier document published on or after the international filing date	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O	document referring to an oral disclosure, use, exhibition or other means	*A*	document member of the same patent family
P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

09 JULY 1997

Date of mailing of the international search report

11 SEP 1997

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